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# Art. X.—*Phosphatic Nodules in the Geelong District.*

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(With Plate XV.)

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## I. Introduction.

In July, 1930, my attention was drawn to the fact that, wherever an outcrop of the remanié phosphatic nodule bed occurs in the Geelong district, it invariably rests on Miocene limestones and beneath Lower Pliocene ferruginous sands. The nodules contain a characteristic fauna of which about 30 per cent. of the identifiable forms are crabs[5], and it soon became evident, that in the numerous outcrops, one was dealing with the same bed. The fact that it was a remanié bed occupying valleys in the Miocene limestone, in contrast with the concretionary nodules, embedded in that limestone, afforded a means of comparing methods of phosphatisation and necessitated an inquiry into the diastrophic phases and palaeogeography of the area.

## II. Remanié Phosphatic Nodules.

The remanié bed, usually fairly horizontal, averages about 2 or 3 inches in thickness; the nodules are not cemented, the interstices being filled with a mixture of sand and quartz pebbles from the overlying ferruginous sands. About 95 per cent. of the fragments in the remanié bed are waterworn nodules of phosphatised sandy limestone, while the remainder includes abraded shells of Ostrea, Cardium, &c., shark's teeth, fragments of cetacean bone, and (at Curlewis) a few pebbles of Older Basalt.

The nodules are suboval with an average shorter axis of from 3 to 6 inches. Most of them are smooth on the outside; some, however, are coated with a white inflorescence; many are pitted. The exterior is usually of a cream or brown colour, but the interior is bluish-brown or grey, and of a fine granular texture. There is a definite relation between the colour and the degree of phosphatisation; hard black nodules contain up to 25 per cent. of $P_2O_5$, brown nodules about 12 per cent., and soft yellow nodules about 1 per cent. or less. Phosphatisation is not always uniform throughout a nodule, and one can distinguish concentric, oolitic, and irregular structures of varying richness.

Mr. J. G. Doyle determined $P_2O_5$ percentages in some remanié nodules with the following results:—

| | Curlewis. | Batesford. | Baker's Bridge. |
|---|---|---|---|
| Relatively rich .. | 24.60 | 20.62 | — |
| Medium .. .. | 18.59 | — | 12.15 |

Mr. J. C. Watson, of the Geological Survey Laboratory, made a complete analysis of a moderately phosphatic nodule from Curlewis, as follows:—

| | per cent. |
|---|---|
| $SiO_2$ .. .. .. | 26.36 |
| $Al_2O_3$ .. .. .. | 2.18 |
| $Fe_2O_3$ .. .. .. | 7.49 |
| $MgO$ .. .. .. | 1.31 |
| $CaO$ .. .. .. | 30.64 |
| $H_2O$ above 110° C. .. .. | 2.50 |
| $H_2O$ below 110° C. .. .. | 0.98 |
| $CO_2$ .. .. .. | 6.20 |
| $P_2O_5$ .. .. .. | 18.59 |
| $TiO_2$ .. .. .. | 0.36 |
| | 96.61 |

Sections of this rock examined under the microscope show that it was originally a sandy limestone or marl, the calcite in which has been almost entirely replaced by amorphous calcium phosphate. The replacement mineral is oolitic in part, and interstitial; it surrounds scattered small angular grains of quartz and dark-brown fragments of shells, tests of foraminifera and other shelly material. In the cavities of the darker shelly fragments were found opaque flakes of carbonaceous matter, and occasionally minute flakes of decolorised biotite. Apart from some small grains of calcite found in the interior of the globular foraminifera, very little calcite is present. On the other hand, in poorly phosphatic nodules, particles of crystalline calcite are fairly common.

The hard parts of crabs are common, and fish scales, cetacean bone, mollusca, polyzoa, and foraminifera fairly common in the nodules.[5] The associated shells are Ostrea, Cardium, and similar stout types; they are all more or less abraded. No true coprolites were found.

## III. Concretionary Phosphatic Nodules.

A. M. Howitt[3] has recorded concretionary phosphatic nodules in soft Miocene limestone at Thompson's Creek, near Moriac, about 16 miles W.S.W. from Geelong. Similar concretionary nodules were found in many of the Miocene exposures near Geelong during the progress of these observations.

They are difficult to distinguish from the containing limestone, the exterior being of the same creamy colour and earthy appearance as the limestone. By fracturing them, however, their greater hardness and internal blue-brown to black colour afford a ready means of detection. They are usually spheroidal, from 2 to 9 inches in diameter, of granular texture, and contain fossils similar to those of the containing limestone.[5]

Often a fossil is found imbedded partly in the concretionary nodule and partly in the containing limestone. A cetacean fragment, a large gasteropod, or the hard parts of a crustacean often form the nucleus of a concretion.

The following estimations of the percentages of $P_2O_5$ in concretionary nodules were made by Mr. Doyle:—

| | per cent. |
|---|---|
| Thompson's Creek .. .. .. | 24.74 |
| "Woodlands," near Moriac .. .. | 23.40 |
| Torquay, near Eagle Rock .. .. | 11.01 |
| Waurn Ponds .. .. .. | 14.99 |
| Western Beach, Geelong .. .. | 17.40 |

In Howitt's paper[3] the percentages of $P_2O_5$ in three samples from Thompson's Creek were given as 22.6, 26.6, and 23.1.

The nodules are thus concentrates, and are chemically very similar to the remanié type—the richest contain about 26 per cent. of $P_2O_5$, the medium about 12 per cent., while the enveloping limestone has less than 1 per cent.

Microscopically these nodules are similar to the remanié type, consisting of amorphous calcium phosphate, calcite, quartz grains and carbonaceous matter, with fragments of shells and foraminifera.

## IV. Method of Phosphatic Replacement.

The mechanism of the growth of concretions is not yet satisfactorily explained. In the present case, a decided concentration of phosphate has taken place, as the following table of $P_2O_5$ percentages in the dried skeletons of some common marine forms, likely to be present in the Miocene limestone, will show:—

| — | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| $P_2O_5$ % | 41·28 | 31·03 | 22·03 | 8·87 | 7·21 | 6·52 | 3·86 | 3·26 | 3·01 | 0·04 |

1. Brachiopod: Lingula. Analyst W. Wheeler(1).
2. Whale, Waurn Ponds. Analyst J. G. Doyle.
3. Mullet, Port Phillip. Analyst Hilda Kincaid(6).
4. Shark, Port Phillip. Analyst Hilda Kincaid(6).
5. Spider Crab: Lithodes. Analyst W. C. Wheeler(1).
6. Blue Crab: Callinectes. Analyst W. C. Wheeler(1).
7. Alcyonaria: Phyllogongia. Analyst W. C. Wheeler(1).
8. Lobster. Analyst W. H. Hudleston(4).
9. Crab. Analyst W. H. Hudleston(4).
10. Oyster. Analyst Hilda Kincaid(6).

With regard to the percentage of $P_2O_5$ in the flesh or muscle of these forms there is little information available, but it is unlikely to exceed 1 per cent. in any case. Hilda Kincaid(6) obtained the following figures for $P_2O_5$ in fresh muscle:—Mullet 0.51 per cent., Oyster 0.57 per cent., Lobster 0.33 per cent.

From the foregoing it appears that the source of the phosphate for the concretions has been the tri-calcic phosphate in the bones and shells of the fossils in the limestone. The solution of such basic phosphate, disseminated throughout a rock, might be brought about by carbonated ground water, especially if the latter contains NaCl or $NH_4Cl$. Bischoff(2) and Rama Rao(8) support this view. Doubtless the decomposition of the protein substances of the entombed forms, particularly burrowing crabs, would produce a certain amount of soluble phosphate, e.g., ammonium phosphate, which when in contact with a suitable calcareous shell would metasomatically replace the carbonate, as has been shown by Renard and Cornet.(7)

Proof that soluble phosphates exist in circulating ground waters was obtained by Mr. G. B. Hope at Demon's Bluff, on the coast about a mile east of the Anglesea River. Here the cliffs are 200 feet high, the surface beds consisting of Lower Pliocene ferruginous sands and gravels, the middle beds of Tertiary carbonaceous sands, and the lowest beds of carbonaceous marls. At certain places on the beach, seepages from the carbonaceous marls occur, and the water in these is highly phosphatic. Nodules of blue-green vivianite, about 3 inches in length, have formed at these seepages. One analysis showed 18.95 per cent. $P_2O_5$ and 26.21 per cent. Fe. The surrounding carbonaceous marl contains only 0.36 per cent. $P_2O_5$. Evidently here the carbonated ground waters dissolved the disseminated phosphate and it became concentrated at the beach level, thus forming the nodules of vivianite.

" The experimental work of Reese on the solubility of calcium phosphate has shown that it dissolves freely in swampy carbonated waters, especially in the presence of decaying organic matter. It is interesting to note that when such a solution is allowed to stand over calcium carbonate, the calcium phosphate is redeposited."(8)

The growth of the calcium phosphate cemented concretions in the Miocene limestones is therefore probably due to the replacement of the carbonate of the argillo-calcareous material surrounding the original nucleus, which is always of a phosphatic nature, e.g., a piece of cetacean bone, the hard part of a crab, or the like.

Replacement is clearly indicated by an analysis made by Mr. Doyle of a concretion taken from a marl pit between Waurn Ponds and Grovedale. This dark concretionary nodule and the yellow limestone immediately enclosing it were partially analysed to ascertain (*a*) the extent of replacement of the carbonate by phosphate, (*b*) if the relatively dark colour of the concretion was due to increase in the iron content.

| | $P_2O_5$ | $CO_2$ | Fe |
|---|---|---|---|
| Dark concretion .. .. | 14.99 | 18.75 | 1.53 |
| Yellow containing limestone .. | 4.32 | 28.48 | 1.55 |

An increase of 10 per cent. in the $P_2O_5$ is thus balanced by a decrease of 10 per cent. in the $CO_2$, indicating proportionate replacement. No increase in the iron content occurred, but there is the possibility that the original iron oxides have formed iron phosphate (dark-coloured) by replacement. Otherwise the dark colour must be ascribed to carbonaceous matter.

## V. Comparison of Remanié and Concretionary Nodules.

Enough has been said to show that the two types are lithologically and chemically strikingly similar. The concretionary nodules are ovoidal or spheroidal in shape, and on the average rather larger than the remanié. Subjected to wave action or tidal scour, they would readily acquire the elongated shape and surface smoothness of the remanié type. Immersion in water would result in the relative bleaching of the remanié nodules.

Palaeontologically the remanié nodules differ from the concretionary type in the preponderance of remains of crabs, though otherwise they are very similar. Often the remanié nodules which contain the crab do not contain any other fossils, and this suggests that the crab is adventitious to the fauna; probably the crab-containing nodules were formed later in the depressions in which the ordinary type of remanié nodules were accumulated.

## VI. Accumulation of Remanié Beds.

The remanié bed always rests on the surface of the Miocene limestones and beneath the Lower Pliocene ferruginous sands, but there are many instances of Lower Pliocene sands resting on Miocene limestones without the intervention of the remanié bed. This is notably the case along the banks of the Leigh River, Sutherland's Creek, Batesford open cut, and the Bellarine Peninsula (east side).

The remanié bed, which is clearly a detrital deposit, outcrops in the banks of Bruce's Creek from Bannockburn to Murghebolue, the banks of the Moorabool River from above Baker's Bridge to Newtown, Western Beach, Fisherman's Gully, Cowie's Creek, and on the western Bellarine Peninsula from Curlewis to Ocean Grove.

An examination of these outcrops shows that the upper surface of the Miocene limestone beneath the nodule bed is always at a lower elevation than that of the general surface of the limestone. It is evident that the nodule bed has been deposited in valleys or depressions due to erosion. The diastrophic phases responsible for this erosion were as follows:—

A. Uplift and emergence of Miocene limestones, and growth within them of concretionary nodules.

B. Erosion of the Miocene limestones, resulting in the removal of the containing limestone and the accumulation of the resistant concretionary nodules in the river valleys.

The valleys never got beyond a juvenile stage; they were still being vertically eroded when they were again submerged. The trend of the remanié beds indicates the courses of the post-Miocene valleys, and these agree approximately with those of the present rivers; furthermore their fall, as indicated by the underlying surface of Miocene limestone, is about the same.

A third diastrophic phase,

C. Slow subsidence and emergence,

involved the drowning of the valleys and the formation of rias or narrow arms of the sea extending for some distance inland and well protected. In these rias detrital nodules and mud accumulated below wave base, and as erosion was checked by the subsidence, the conditions of sedimentation were placid. In the finer mud were the burrows of the mud-haunting crabs,

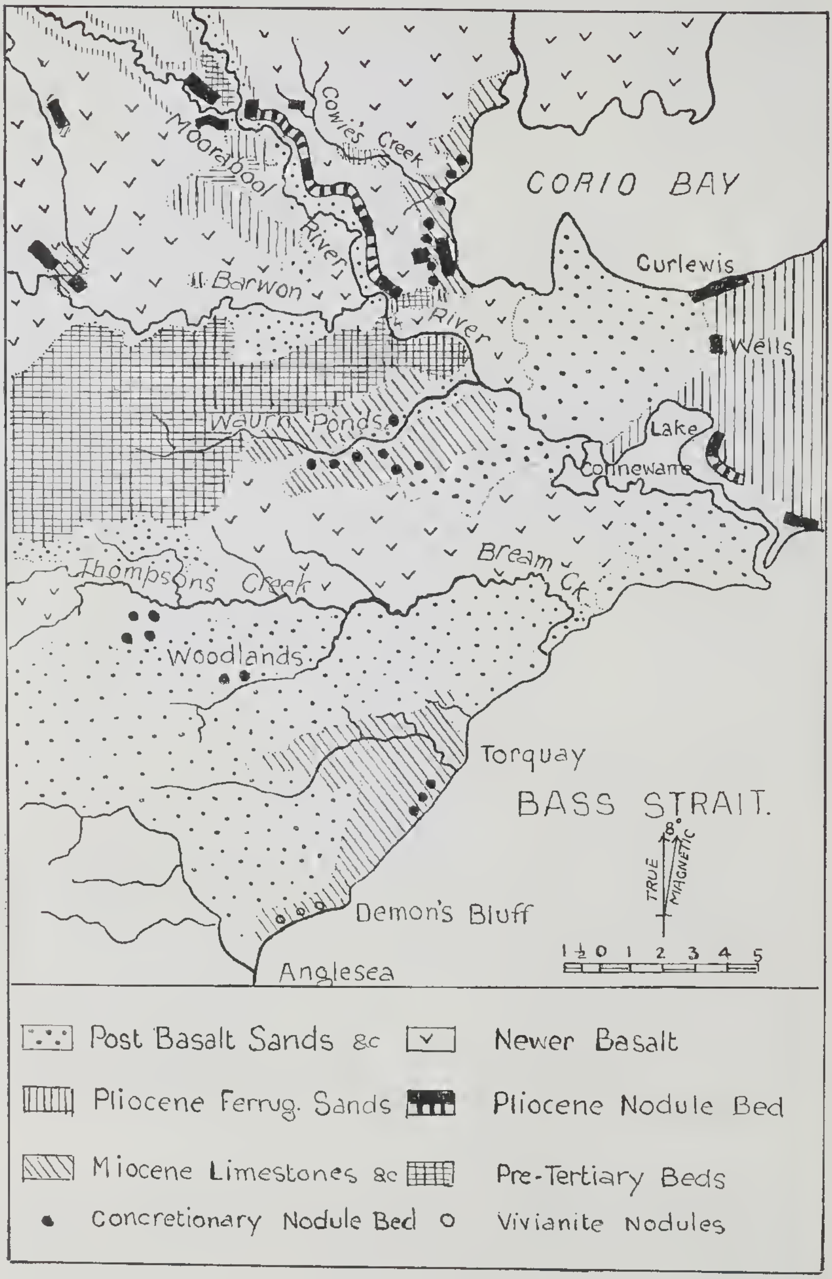
Moorabool River
Cowie's Creek
CORIO BAY
Barwon River
Curlewis
Wells
Waurn Ponds
Lake Connewarre
Thompsons Creek
Bream Ck
Woodlands
Torquay
BASS STRAIT.
TRUE
MAGNETIC
8°
Demon's Bluff
Anglesea
1½ 0 1 2 3 4 5
Post Basalt Sands &c
Newer Basalt
Pliocene Ferrug. Sands
Pliocene Nodule Bed
Miocene Limestones &c
Pre-Tertiary Beds
Concretionary Nodule Bed
Vivianite Nodules

FIGURE 1.

and as these died they formed calcium phosphate cemented nodules of considerable richness, up to about 8 per cent. $P_2O_5$. Such nodules have not been further enriched.

The fourth diastrophic phase,

D. Gradual uplift,

brought the accumulated sediments within wave base, and caused their disintegration. The fragments were rolled and accumulated to form the remanié bed as it now outcrops. An extension of this phase was

E. Complete emergence,

and the resumption of terrigenous conditions which marked the beginning of the deposition of the Pliocene ferruginous sands. Owing to the ease with which the Pliocene sands could be eroded,

F. A post-Pliocene cycle of erosion

cut valleys in them. This cycle was terminated by the

G. Newer Basalt,

which filled the valleys and initiated

H. The post-Newer Basalt cycle,

characterised by erosion on the flanks of the infilling basalt. This cycle is still in progress, and by deep vertical erosion the remanié beds resting on Miocene limestones and beneath Older Pliocene ferruginous sands have been exposed.

The exposure of the remanié beds is therefore dependent on the post-Miocene cycle of erosion, subsidence, sedimentation, uplift and subsequent erosion. Their extent is limited to the valleys of the post-Miocene cycle, and their exposure to the post-Newer Basalt erosion.

If an area was on the watershed during the post-Miocene cycle no remainié nodule bed will be found. Thus the Dog Rocks during the post-Miocene cycle was almost certainly a watershed; hence we do not see the nodule bed in the open cut at Batesford.

## VII. Conclusions.

The Miocene limestone and marl of the Geelong district contains concretionary phosphatic masses, from 2 to 9 inches in diameter, which contain fossil organisms of the same character as the containing limestone. The phosphate is amorphous, and the growth of the phosphate concretions is due to the replacement of the calcium carbonate around the nuclei by phosphate carried in solution by carbonated ground waters.

Resting on the Miocene limestone, and beneath the Lower Pliocene sands, is a thin bed of rolled phosphatic pebbles, the remanié bed. Lithologically and chemically the remanié nodules are identical with the concretionary nodules, and palaeontologically they are very similar. They represent residual concretionary nodules from which the containing limestone has been removed. Associated with these nodules are abraded Miocene shells which are also remanié from the erosion of the limestone. Many of the nodules contain fossil crabs exclusively, and these were later formed, probably during the accumulation of the remanié bed.

The following diastrophic phases are involved in the formation of the nodule bed and its subsequent exposure:—

(*a*) Uplift and emergence of the Miocene limestone.
(*b*) Erosion of post-Miocene valleys.
(*c*) Slow subsidence and invasion of sea.
(*d*) Gradual uplift. Complete emergence.
(*e*) Deposition of Pliocene sands.
(*f*) Erosion.
(*g*) Newer Basalt flows.
(*h*) Formation of flanking valleys and exposure of remanié nodule bed by vertical erosion.

On account of its small size the remanié bed is of no economic value. Likewise the concretionary nodules are too few and scattered to repay collection. There may be some slight value in the low grade phosphatic marls of the Anglesea district, but at present this region is too remote from a market.

## VII. Acknowledgments.

My sincere thanks are due to Mr. G. B. Hope, B.M.E., who introduced to me the problem of the origin of the remanié bed, and assisted me throughout the work. I am also indebted to Mr. R. A. Keble, F.G.S., of the National Museum, for identification of fossils(5) and criticism of the form of this paper. The informative analyses made by Mr. J. G. Doyle, of the Gordon Institute of Technology, and Mr. J. C. Watson, of the Geological Survey Laboratory, proved very useful, as also did the rock sections prepared for me by Prof. Skeats and Mr. D. J. Mahony. Lastly, I would thank Messrs. A. M. Howitt, J. M. Hennessy, R. McSweeney, and J. M. Hobba for their help in various ways.

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Remanie' Nodule Bed exposed in road cutting, Fyansford Hill, Geelong.

Typical Remanie' Nodules from Curlewis.